



Direct measurement of oleate adsorption on hematite and its consequences for flotation



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ARTICLE INFO

Keywords:

Oleate adsorption
Hematite
Flotation

ABSTRACT

The direct measurement of adsorbed oleate onto hematite removes the uncertainty of depletion of oleate onto non-hematite surfaces. Direct measurement of oleate onto hematite at pH 4 and as a function of pH at constant oleate addition was made using Differential Scanning Calorimetry. Oleate adsorption measurements were conducted on conditioned, concentrate and tailing samples, corrected for their surface areas. Adsorption measurements were complemented by flotation tests. At pH 4, oleate adsorption on conditioned samples reached a complete monolayer by vertical orientation at the critical micelle concentration (CMC) of the oleate. The onset of multilayer adsorption by vertical orientation on the concentrate samples was determined at the CMC, and monolayer coverage on the non-floated material was always less than one monolayer under two-point and vertical oleate orientation. Flotation recovery of hematite at pH 4 remained high under equilibrium oleate concentrations above the critical hemi-micelle concentration of oleate. Oleate adsorption on hematite as a function of pH showed maxima at pH 4 and 9, suggesting co-adsorption of molecular and ionic oleate species at pH 4. Hematite flotation with 10^{-4} molar oleate addition was high for pH values above 4.

1. Introduction

It is the aim of this paper to complement and extend a previous article by the author that was presented at the XXV International Mineral Processing Congress held in Brisbane, Australia in 2010 and published in the Congress Proceedings (Quast, 2010). In that paper the interaction of a technical grade sample of sodium oleate with the hematite surface was determined using differential thermal analysis, in that case, Differential Scanning Calorimetry (DSC). The advantage of this technique is that it measured the actual amount of oleate adsorbed on the surface directly, and did not suffer from the complications associated with indirect methods (e.g. depletion of reagent from solution, uncertainty of oleate adsorption onto other mineral surfaces and walls of container), where the amount adsorbed was calculated from the difference between initial and final values of oleate in solution. In order to limit the scope of this paper, the discussions will be primarily confined to the hematite-oleate system.

It can be hard to quantify removal of oleate as precipitate and on surfaces other than the hematite, as discussed by Morgan et al. (1986). The initial data reported by Morgan et al. (1986) showed maximum oleate depletion at pH 2–3, which corresponded to no hematite flotation. This was explained by the effects of centrifugation on suspended oleate colloidal complexes, surface and bulk precipitation, adsorption on the test vessel and the mineral bed and the amount associated with

the rinse water, all of which did not contribute to the hydrophobicity of the hematite. A similar mismatch between oleate adsorption as measured by solution depletion and flotation for the hematite-oleate system was reported by Kulkarni and Somasundaran (1980) where maximum oleate adsorption was noted at pH 3 which corresponded to virtually no flotation for oleate additions of 1.5×10^{-5} molar oleate at 75 °C. A flotation maximum was recorded at pH 7.5, which was attributed to the maximum concentration of the oleate acid-soap moiety in solution.

In commenting on these discrepancies between adsorption of oleate and corresponding hematite flotation, Chanturia and Kondrat'ev (2014) suggested that mineral flotation is not governed by the adsorption density of the reagent but by the presence of the specific forms of the reagent to break the water film around the mineral particle and then remove it. These authors maintain that the amount of reagent on the mineral surface is of no importance, but the properties of the reagent are critical. This leads in to the concept that the oleate acid-soap is the most important solution moiety, and maximum flotation occurs when the concentration of this species is a maximum as reported by Kulkarni and Somasundaran (1980).

Subsequent work by Morgan et al. (1987) investigated the significant effects of the solid/liquid ratio on oleate adsorption onto hematite. Adsorption density extracted from total oleate depletion was found to be quite low, less than 1% surface coverage. To explain the high hydrophobicity at such low adsorption, a mechanism involving

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<https://doi.org/10.1016/j.mineng.2017.12.011>

Received 18 September 2017; Received in revised form 22 November 2017; Accepted 11 December 2017

Available online 02 February 2018

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two-point attachment was proposed.

In the previous paper by the author (Quast, 2010), the mechanism (s) of attachment of sodium oleate under varying solution concentrations was analysed and discussed at pH 7. The results indicated that the orientation of the adsorbed collector was dependent on its equilibrium solution concentration and proceeded from horizontal to two-point and finally to vertical orientation with increased oleate addition. Under horizontal orientation, the hydrocarbon chain was oriented parallel to the hematite surface. With two-point orientation, the collector was attached via the double bond in the hydrocarbon chain plus through the carboxyl group. Vertical orientation means that the collector was attached via the carboxyl group, with the hydrocarbon chain oriented perpendicular to the surface of the hematite. Good correlation between collector adsorption and flotation recovery was demonstrated.

The same technique was used in this paper, but the first series of tests was conducted at pH 4, where the hematite surface would be positively charged, and oleate would be predominantly in undissociated form. Another series of tests was conducted across a broad pH range (2–10) at a constant initial oleate addition corresponding to 10^{-4} molar.

It is not the purpose of this paper to describe the hematite-oleate system in detail, as it has been the subject of a number of papers by the author (Quast, 1999, 2015a, 2015b, 2016a, 2016b, 2016c, 2017a, 2017b; Joseph-Soly et al., 2015) which may be consulted for further information. It was found that both oleate solution chemistry and mineral surface characteristics dominated the flotation behaviour of hematite, with maximum flotation recoveries obtained at neutral pH values, close to the zero point of charge of the mineral. Chemisorption was confirmed as the dominant mechanism of oleate adsorption on the hematite surface, although physical adsorption of oleate can make a contribution, particularly at lower values of pH. The region of significant hematite flotation with oleate often corresponded to the region of stability of the ferric oleate complex (Joseph-Soly et al. 2015). The pH curves for the recovery of hematite using oleate (e.g. as reported by Quast, 2016a) correspond closely with that for the contact angle of soap (specified as oleate) on hematite as a function of pH published over 70 years ago (Taggart and Arbiter, 1943).

The technique used in the previous study (Quast, 2010) and this study was based on the work of Howe and Pope (1970/71) who used Differential Thermal Analysis (DTA) to measure the amount of collector on the surface by the area on chart paper of the peak when the collector burnt. The technique of DSC utilises measuring the difference in energy input to the sample and the reference material when they are heated at a constant rate of temperature increase. When the collector ignites, considerable energy must be supplied to the reference in order to maintain both the sample and the reference at the same temperature. This change in energy requirement can be measured very accurately; hence low collector coverages can be quantitatively determined.

2. Literature review

The references pertaining to the adsorption of oleate on hematite are discussed under the sub-headings pertaining to their methods of measurement. The rationale for using direct rather than indirect measurements has been discussed in the previous section.

2.1. Hydrophobicity of the hematite surface

The natural hydrophobicity of the hematite surface is relatively low. As discussed in a recent article by the author (Quast, 2017b), the contact angle for the surface of hematite in the absence of surfactants is often in the range 45–55°, but can span a wide range of 30–79.5° (Iveson et al. 2000, 2004, Mao et al. 2013). The contact angle for hematite in contact with oleate is much higher, with values of 88° (e.g. Iwasaki et al. 1960, Rath et al. 2014, Abaka-Wood et al. 2017). This shows that some form of surfactant is required to increase the contact

angle on the natural hydrophilic hematite surface to make it respond to flotation.

2.1.1. Infrared spectroscopy

The classic reference for the adsorption of oleate onto hematite was published by Peck et al. (1966). These authors used infrared spectroscopy to study the adsorption of oleate on three varieties of hematite (red mineral hematite, specular hematite and synthetic hematite). Each of the minerals reacted with either oleic acid or a solution of sodium oleate to form a mineral cation-collector anion chemisorbed layer at the solid-liquid interface. Evidence was presented which showed that molecular filming on the mineral surfaces with undissociated oleic acid preceded chemisorption. Infrared absorbance data was collected over the pH range 5–9, and showed a maximum in absorbance of oleic acid close to the isoelectric points of the hematites. For the specular and red hematites, maximum adsorption occurred at pH 8. Flotation recovery was closely related to the concentration of chemisorbed oleate on the mineral surface. Physically adsorbed oleate on the red hematite decreased linearly as the pH of the suspension was raised from 4 to 8, being zero at pH 8.

Uwadiale (1992) questioned the interpretation of the infrared data of Peck et al. (1966) to elucidate the mechanism of oleate adsorption on hematite. His examination of the spectra of the test samples showed that no adsorption of oleate or oleic acid on ferric oxide occurred at pH 7.5 and 9.5, and the adsorption at pH 4 involved the physical adsorption of molecular oleic acid. Peck et al. (1966) reported that the adsorbed oleic acid and sodium oleate on their test samples were not desorbed with water or absolute alcohol prior to drying and infrared analysis. It is thus possible that many of the samples scanned may contain physical mixtures of oleate and hematite (or ferric hydroxide). Uwadiale (1992) also questioned if chemisorption, unlike physical adsorption, was independent of the isoelectric point, why the specificity of pH values at which the different types of natural or synthetic hematite reacted chemically with sodium oleate or oleic acid? Electrophoretic measurements do confirm the adsorption of oleate on hematite as via chemisorption (e.g. Quast, 2016b).

Akhtar (1973) plotted the infrared absorbance at 1410 cm^{-1} from the hematite-oleate internal reflectance spectrum as a function of pH from pH 7–10, and showed how it was parallel to the oleate flotation data of hematite as previously reported by Peck et al. (1966). This frequency was suggested as the result of the superposition of CH_3 , CH_2 deformation bands on symmetric stretching of the COO^- group.

Gong et al. (1991) used Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT) to analyse the adsorption of oleate on hematite between pH values 6.0 and 9.8. The spectra suggested that chemisorption of oleate on hematite took place under all the experimental conditions and that the chemisorbed species were either chelating bidentate or bridged bidentate. The bridged bidentate configuration should correspond to a vertical orientation of adsorbed oleate, with the chelating bidentate probably representing two-point orientation. Dimers of oleic acid coexisted with the chemisorbed oleate. Maximum adsorption of all species occurred at pH 8. Khalil et al. (2014) used FTIR to investigate the adsorption of oleate on hematite nanoparticles. Their data indicated that the binding mechanism between the oleic acid and the hematite surface was by monodentate interaction.

2.2. Radiochemical methods

Okon and Salman (1966) measured the adsorption of C^{14} labelled oleate at pH 10 onto a sample of 75–100 μm hematite with a surface area of $0.1035\text{ m}^2/\text{g}$. They reported that the amount adsorbed steadily increased up till about twice the value of the CMC, then rapidly increased as the oleate solution concentration increased further. Plotting the data on logarithmic coordinates showed a change in slope from 0.5 below the concentration where the adsorption increased rapidly to a much higher slope. Hallimond tube flotation showed a maximum at a

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